PARAMAGNETISM OF SINGLE CRYSTALS OF THE SALTS OF THE IRON GROUP OF ELEMENTS AT LOW TEMPERATURES—PART I—THE IONIC SALTS OF THE F-STATE IONS Cr^{+++} AND Ni^{++}*

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ABSTRACT. In the first few sections of the paper a critical discussion of the existing theories of paramagnetic salts and experimental data supporting the crystalline electric field theory of paramagnetic salts developed by Van Vleck, Bethe and Penney and Schlapp, are given. In the latter parts, experimental data on the anisotropies and effective moments of several six-coordinated nickel salts at various temperatures, in the range of 300°K and 80°K, attained with a specially devised cryostat by the author, are given and discussed on the basis of the electric field theory. Assuming the electric field in these crystals to be predominantly cubic, with a small superimposed rhombic component, the basic $^3F_4$-state of the Ni^{++} ion splits up into a Stark-pattern, consisting of a singlet and two triplets with a mean separation of about 20,000 cm^{-1} due to the cubic field; the components of the triplet being separated to a much smaller extent by the rhombic field. In the six-coordinated nickel salts the cubic field constant D, has a positive sign and in such a field the singlet level is the lowest lying in the Stark-pattern. Consequently in such salts we should expect the Ni^{++} ion (1) to have approximately a 'spin only' value for the effective magnetic moment, (2) to obey the Curie Law of temperature variation of the susceptibility closely and (3) to have a feeble anisotropy. In the Ni^{++}, however, the spin orbit coupling is fairly strong, about -335 cm^{-1}, and hence the effect of the crystalline field on the spin moments will be quite large by virtue of the coupling of the spin moments with the orbitals which are themselves strongly affected by these fields. In addition to this the contribution from upper cubic levels will also be appreciable. With the help of our experimental data we have calculated the cubic and rhombic field constants for Ni^{++} salts and have made a detailed consideration of the relative contributions of the various factors towards the total effective magnetic moment. The anisotropies and the effective moments and their temperature variations agree perfectly with the theoretical calculations of Penney and Schlapp. The field constants calculated are found to be practically independent of temperature, as is to be expected in view of the strong binding between the Ni^{++} ion and its neighbouring co-ordination group. It is also possible to calculate the spin-orbit coupling constant λ, for Ni^{++} ion purely from magnetic data and these calculated values agree fairly with the spectroscopic value. A similar treatment for the Cr^{+++} ion which is in the $^4F_{3/2}$-state leads to the conclusion that here contributions from other sources than the spin moment towards the effective moment is of very much less importance and in consequence the salts have much less anisotropy and obey Curie Law almost perfectly.

GENERAL THEORY OF PARAMAGNETIC BEHAVIOUR

1 *Elementary Magnets Free*

All theories of paramagnetism are based on the finding that the ultimate particles in the paramagnetic substances, namely the atoms, ions or molecules, as

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It must be remembered, however, that the deviations from the Curie Law are more or less common among the paramagnetic substances, particularly in the solid and the liquid states, (Stoner, 1934) and it is only in a few cases like those considered above that the deviations can be explained on the basis of such "over-lapping" of the multiplet intervals. For example, the salts of the iron group of elements, in which the multiplet intervals for the free ions are moderately large, do show considerable deviations from the Curie Law even when allowance is made for the overlapping of the levels. We have, therefore, to invoke, in general, for the explanation of these deviations, the restrictions that would be imposed in these media on the freedom of rotation of the elementary magnets.

2. The Weiss Law of Temperature Variation of Susceptibilities

It is well-known that the temperature variation of the susceptibilities of many of these paramagnetic substances particularly at high temperatures is given by the relation,

$$\chi = \frac{C}{T-\theta} \qquad \ldots \quad (6)$$

where θ, is a small characteristic temperature for the substance; which reminds us of the similar behaviour of the ferromagnetic substances above their Curie points. This suggests at first sight that in these paramagnetic substances also, the deviation from the Curie Law is due to the same type of "inner fields", which explain the behaviour of ferromagnetics both above and below their Curie temperatures and which has been since known to arise from the Heisenberg "exchange interaction" between the spin moments of the magnetic particles. This surmise, however, is not justified for the following reasons.

Firstly, large values of θ occur even in such highly magnetically dilute salts as Tutton salts in which the ferromagnetic interactions should be negligible. Secondly, in these paramagnetic substances both positive and negative values of θ are observed and further, ferromagnetism does not occur even below the value of θ, where positive, as deduced from measurements of susceptibilities at high temperatures.* Actually, at temperatures near about θ, the deviations from the Curie Law become quite complicated and is another reason against accepting the ferromagnetic "inner field" as the cause of these deviations.

Indeed, the validity of a law of the type (6) limited to high temperatures only, $T >> \theta$, has not much significance, since then a small deviation from Curie Law, *whatever its origin*, can be expressed by the power series

$$\chi = \frac{C_1}{T} + \frac{C_2}{T^2} + \ldots\ldots \qquad \ldots \quad (7)$$

* The ferromagnetism observed by Simon in some of the ordinary paramagnetics at very low temperatures of the order of 0.1 °K, is presumably due to the mutual influences of the elementary magnets, owing to their close proximity at such low temperatures, and is quite unrelated to the above large deviation from the Curie Law (1936, *Comptes Rendus*).

For large values of T, for which only Weiss Law is obeyed experimentally, the series reduces to a first approximation to

$$\chi=\frac{C_1}{T-\theta}, \quad \theta=\frac{C_2}{C_1}\ldots\ldots \qquad \ldots (8)$$

Thus a proper experimental verification of the law of the type (6) can be made only at temperatures *comparable to* θ, and it is precisely here the law fails experimentally.*

Thirdly, an inner field of the exchange type cannot explain how in some salts, *e.g.*, Cr^{+++} and Ni^{++}, which closely obey the Curie Law and in which therefore the elementary magnets may be presumed to be free, the effective moments of the elementary magnets Cr^{+++} and Ni^{++} instead of being the free ion values, are experimentally found to be such as appear to arise—as has been pointed out by Sommerfeld (1923), Bose (1927) and Stoner (1929)—mostly out of the spin moments of the electrons; as if the orbital moments have become in some way quenched. On the other hand, it is also to be noted that the deviations from the Curie Law are the largest where the effective magnetic moments have large orbital contributions, *e.g.*, in the salts of Fe^{++} and Co^{++}. Fourthly, the "inner field" theory fails also to give any explanation of the large magnetic anisotropy that is observed in many paramagnetic crystals, the variation of this anisotropy with temperature and its relation to the orbital moments.

Thus an "inner field" of the exchange interaction type cannot explain the observed deviations from the behaviour to be expected from the free magnetic particles, at any rate in the highly diluted paramagnetic salts; though in substances like the anhydrous chlorides or oxides and similar compounds of the transition elements, due to high concentration of the magnetic particles, the exchange forces also may have an appreciable influence on the magnetic behaviour. (Starr, Bitter and Kaufmann, 1940)

3. *The Influence of the Crystalline Electric Fields on the Paramagnetic Behaviours*

It should be remembered that any alternative to the 'inner field' theory must explain the following outstanding experimental facts satisfactorily :

(1) The deviations from the Curie Law of temperature dependence which at low temperatures become complicated.

(2) The part played by the orbital angular momentum of the elementary magnets in connection with these deviations.

(3) The magnetic anisotropies of single crystals and their intimate relation with the deviations from the Curie Law.

(4) The relative contributions of the spin and the orbital moments towards the total effective moments of the magnetic particles.

* These failures have been referred to in the literature of the subject as 'cryomagnetic anomalies' (Stoner, 1934).

(5) The peculiar magnetic properties of the complex salts of the transition elements whose susceptibilities are in general much lower than those of the corresponding ionic salts and sometimes even diamagnetic.

In recent years the theoretical investigations of Bethe (1929, 1932), Van Vleck, (1932) Penney and Schlapp (1932) and others have thrown considerable light on the nature of the mechanism responsible for restraining the freedom of orientation of the elementary magnets ; and just such a mechanism as would explain the above facts has been found to exist in the strong and asymmetric electric fields that would obtain in the neighbourhood of the paramagnetic ions in the substances that we are considering.

Under the action of such an electric field the $(2J+1)$-fold degeneracy, corresponding to any particular value of the total quantum number J, existing for an assemblage of free paramagnetic ions in the absence of a magnetic field, will be already removed, at least partially, even before the incidence of the magnetic field.

This will be in effect a Stark-splitting of the energy states of the paramagnetic ions. In many of the paramagnetic salts the electric field will be sufficiently strong to break down the L-S coupling and further to produce a large separation compared to kT, of the $(2L+1)$ orbital levels ; $(2S+1)$-fold spin degeneracy of each of these orbital levels will, however, be practically entirely left over. The result will be that when a magnetic field is put on, it is only the spin moments of the paramagnetic ions that will be capable of turning round in the magnetic field and contributing to the observed paramagnetism of the medium, whereas, the orbital part of the moment will be more or less completely *frozen*. But though the orbital moments are in this manner prevented from contributing to the effective magnetic moment of the ions, they will still have profound influence on the susceptibility of the medium in the following manner. Though the spin moments are to a first approximation unaffected by the crystalline electric fields, their freedom of orientation in the magnetic field, however, will be very much hampered indirectly through their coupling with the orbital moments, which are themselves strongly affected. This will in effect be equivalent to the imposition on the spin moments, of local restraining fields magnitude of which will depend on the orbital moments and the strength of the spin-orbit coupling. Such 'local fields' besides having an essentially different origin from Weiss 'inner fields', differ from them also in other important respects. Whereas, the 'inner field' in Weiss theory is proportional to the intensity of magnetization thus leading to an expression of the type, $\chi=C/(T-\theta)$, which should hold at *all* temperatures greater than θ, the local fields meant to replace the crystalline electric fields will be proportional to the intensity of magnetization as a rough approximation only at temperatures T much greater than θ. This is very satisfactory, since then the $\chi=C/(T-\theta)$ will be valid only at $T>>\theta$ and will break down at low temperatures just as is required by experimental results.

It will be further seen that if we still choose to think in terms of formula (6), the value of C will be determined chiefly by the spin moment of the magnetic particles while the orbital moments will play an important role in determining θ. Thus, as we have mentioned earlier, the susceptibility of the medium which depends on C and θ, will depend not only on the spin moments which contribute to the effective moment but also on the orbital moments which are apparently frozen. The important role played by the orbital moment in determining the susceptibilities was missed in the earlier theories since its influence is confined nearly entirely to θ, the origin of which was previously ascribed to 'inner fields' the nature of which was not properly understood.

Again, the crystalline electric field cannot produce magnetisation by itself since its effect ultimately is merely to quench directly the orbital moments and introduce indirectly large restrictions in the form of local fields on the spin moments. These fields, therefore, cannot lead to the development of ferromagnetism like the 'inner fields' contemplated in Weiss theory.

Lastly, these local fields, intended to replace the asymmetric crystalline fields, will naturally partake of the symmetry of these latter fields and will account for the observed magnetic anisotropies in crystalline media, whereas, the exchange forces are incapable of producing any anisotropy.

So far we have considered the splitting of the energy levels by the crystalline electric fields which are sufficiently strong to break the spin-orbit coupling, but not strong enough to break the Russel-Saunders coupling altogether which is the case for the ionic salts of the iron group with which we are mainly concerned in the present paper. But it should be mentioned here that many cases are known, as for example, some of the complex salts like potassium ferricyanide, potassium ferrocyanide, etc. in which, owing to the close proximity of the negative charges surrounding the paramagnetic ion much closer than in the ordinary ionic salts, the electric fields become sufficiently large to break even the Russel-Saunders coupling and all the l-moments as well as the s-moments of the electrons in the incomplete shell of the individual paramagnetic particles responsible for their magnetism, will be quite independent of each other. Under the influence of the electric field, $(2l+1)$-fold degenerate energy level occupied by the electrons will be split up into as many different levels, each with a two-fold spin-degeneracy and the various electrons in the incomplete shell of the magnetic particle will be accommodated in these levels, of course in accordance with the Pauli Exclusion Principle. The effective magnetic moment will evidently depend on the relative separation of these levels, which ultimately will be determined by the magnitude and asymmetry of the crystalline field involved.

Cases also are known, for example, in the rare-earth salts in which owing to the screening effect of outer completed shells of electrons, the influence of the electric fields on the inner incomplete $4f$-shell responsible for paramagnetism of these salts is not strong enough to break down completely even the L–S

coupling. In such a case we cannot separate out for discussion the spin and orbital degeneracies but will have to regard the energy levels as having a $(2J+1)$-fold degeneracy, *some* of which will be removed by the crystalline field and whatever degeneracy is left over will be removed on the application of a magnetic field. This would account for the deviations from normal paramagnetic behaviour.

4. *Earlier Experimental Evidence for the General Validity of the Electric Field Theory*

The electric field theory has received considerable support from magnetic studies especially those made recently on the crystals of the salts of the rare-earth and the iron group of elements with the latter of which we are concerned.

(1) For the S-state ions, where there are no orbital moments to be quenched, the splitting of the spin levels under the influence of the electric fields will be extremely small. The three principal susceptibilities of the single crystals should then conform, as Van Vleck and Penney (1934) have shown, to expressions of the type,

$$\chi_i = \frac{C}{T}\left(1+\frac{\theta_i}{T}\right), \quad i=1, 2, 3 \qquad \ldots \quad (9)$$

where θ's are very small, of the order of 0.1°K and the sum of the three θ's should be equal to zero. The mean susceptibility will therefore conform almost accurately (*i.e.* upto $1/T^2$ terms at least) to the simple Curie Law, and even for the three principal susceptibilities the deviation from the Curie Law will be very small. These results are verified experimentally in the case of salts of Gd^{+++} ion ($^8S_{7/2}$-state) and Mn^{++} and Fe^{+++} ions ($^6S_{5/2}$-states) in the powdered state (Stoner 1934 ; Leiden Comms.) as also in the state of solution (Bose 1935). It is further found experimentally that the single crystals of these salts have very small but finite magnetic anisotropies as required by (9) and correspond to splitting of the spin levels of the order of 0.1°K (Krishnan and Banerjee, 1936) which can also be obtained independently (Kürti and Simon, 1935) from specific heat measurements of these salts at low temperatures and also from experiments on cooling produced in them by adiabatic demagnetization. Further, at all ordinary temperatures the anisotropy varies as $1/T^2$ as required by (9) (Krishnan, Mukerji and Bose, 1939).

As has been already mentioned, the indirect influence of the crystalline electric fields on the spin moments, through their coupling with the orbital moments which are themselves strongly affected, is evidenced by the deviations from the Curie Law or by the anisotropies exhibited by the single crystals of these substances, which should therefore be a measure of the strength of the spin-orbit coupling. It has been actually possible to calculate the

strength of the coupling in Ni^{++} salts (Krishnan and Bose, 1938, 1939) where conditions are favourable for such calculations.

A particularly striking achievement of the electric field theory (Van Vleck, 1932 ; Penney and Schlapp, 1932 ; Görter 1932) lies in the finding (*a*) that in a given field the Stark-pattern for Co^{++} ion ($^4F_{9/2}$-state) is inverted with respect to that of Ni^{++} ion ($^3F_4$-state) and (*b*) that as one passes from tetrahedral four-coordinated to octahedral six-coordinated salts the potential at the central paramagnetic ion changes sign which is equivalent to an inversion of the Stark-pattern. From this point of view the magnetic properties of six-coordinated Co^{++} and Ni^{++} salts should be very different from each other and further the four-coordinated Co^{++} salts should behave similarly to the six-coordinated Ni^{++} salts and vice versa. These results have been verified experimentally with the six-coordinated Co^{++} and Ni^{++} salts as also with the four-coordinated Co^{++} salts Cs_2CoCl_4 and Cs_3CoCl_5 (Krishnan and Mukherji 1938).

Again, in the case of single crystals of $CuSO_4, 5H_2O$, from the known X-ray fine structure of the crystal, (Beevers and Lipson, 1934) it is possible on the basis of the electric field theory to locate the directions of the principal magnetic axes in the crystal, and to predict that though the crystal is triclinic it is nearly uniaxial magnetically. Both these predictions are fulfilled (Krishnan and Mukherji 1936, 1938).

Further, these large internal electric fields required by the theory are consistent with the known distribution of the charged atoms immediately surrounding the paramagnetic ions in the solid state (Hoffmann, 1931 ; Beevers and Lipson, 1934 ; Hendricks and Dickinson, 1927 ; Chrobak, 1934) and fields of the same magnitude can even exist in the liquid or solution state. For, according to a well known theorem of Jahn and Teller (1941) the distribution of the charged atoms immediately surrounding a given ion is conditioned by the quantum state of the ion itself and has to be such that the resulting electric field should remove wholly the orbital degeneracy of the ion. This would explain satisfactorily the large deviations from the Curie Law of the same order as in solids, observed for paramagnetic salts in aqueous solutions (Stoner, 1925). Evidence for such large Stark-splittings of the energy levels of the paramagnetic ions in aqueous solutions are forthcoming from the observations on the absorption spectra (Spedding, 1937,38 ; Freed, 1938 ; Bose, 1938,39) and the large magnetic birefringence (Chinchalkar etc. 1931-35) of these solutions.

EXPERIMENTAL METHOD

1. *Cryostat*

For the purpose of experimental investigations on magnetic behaviour of single crystals at low temperatures a suitable cryostat was devised by the author, a detailed description of which has already been given in an earlier paper (Bose, 1948). The cryostat was of the gas flow type, the cryostat

chamber being cooled by a flow of cold air through it. The efficiency of cooling and uniformity and steadiness of temperature in the chamber were very high due to the combined action of several factors namely: (1) a proper exchange of heat between the flowing gas and the walls of the chamber by making the flow of the gas turbulent by its passage through a series of suitably arranged perforated copper discs, (2) a thorough conduction of heat by making the walls and the discs of copper sheet and providing a large surface of contact between the gas and these copper surfaces, (3) a suitable thermal capacity of the chamber (4) an efficient automatic relay system for regulating the flow of cold gas through the chamber, controlled by a sensitive constant volume air thermometer incorporated in the chamber. Thus the temperature inside the crystal chamber could be maintained steady to about 0.01°K at any desired value between 300°K and 80°K over long periods, to enable magnetic measurements to be made.

2. *Notations Adopted for Magnetic Measurements*

We adopt here the same notations as used by Krishnan and his co-workers (1932-39) for denoting the magnetic constants of crystals.

In monoclinic crystals the two principal susceptibilities in the (010) plane are denoted by χ_1 and χ_2 respectively, χ_1 being the greater of the two, and the inclinations of the χ_1 axis to 'c' and 'a' axes are given by ψ and $\beta-\psi$ respectively, where β is the obtuse angle between 'a' and 'c'. Further, we denote the angle between χ_2 and 'a' axes by θ, so that $\beta=\pi/2+\theta+\psi$. The susceptibility along the 'b' axis is denoted by χ_3. In the orthorhombic crystals the three principal magnetic axes will evidently be the crystallographic axes 'a', 'b' and 'c' axes and the principal susceptibilities measured along these axes will be denoted by χ_a, χ_b and χ_c respectively. In the tetragonal, hexagonal and trigonal systems the crystallographic symmetry axis 'c' will evidently be also an axis of rotational magnetic symmetry and we shall denote the susceptibility along this axis by $\chi_\parallel$ and that in the perpendicular plane by χ_1.

Our magnetic measurements consist of firstly, locating one of the magnetic axes if it is not already known from crystal symmetry, from which the direction of the other two can be easily found out, and then determining the principal anisotropies $\chi_1-\chi_2$ and $\chi_1-\chi_3$, from measurements on anisotropies in any two known planes in the crystal. For the uniaxial crystals evidently, only one such measurement is needed to determine $\chi_\parallel-\chi_1$. Secondly, the absolute susceptibility along any known direction of the crystal is determined, which combined with the anisotropy measurements, gives us the values of all the three principal susceptibilities.

3. *The Measurement of Magnetic Anisotropies*

The principle underlying these measurement is the same as in our earlier works and the details of the actual technique are given in the paper

mentioned in a previous section. The crystal is suspended in a horizontal homogeneous magnetic field with a fine quartz fibre suspension from a torsion head and so adjusted that the torsion on the fibre is zero. Starting with this position the torsion head is rotated through a critical angle α_c and the crystal follows through a smaller angle $\pi/4+\sigma_c$, such that the equilibrium of the crystal in the field becomes unstable and the crystal turns round suddenly. It can then be shown that the anisotropy, $\Delta\chi$, of the crystal in the horizontal plane is given by

$$\frac{1}{2}\cdot\frac{m}{Mc}\cdot H^2\Delta\chi=\chi\ (\text{say})=\frac{\alpha_c-\pi/4-\sigma_c}{\cos 2\sigma_c} \qquad \ldots\ (10)$$

where $\sin 2\sigma_c=1/2\lambda$.

In the above equation m is the mass of the crystal, M its gm. molecular weight, H the magnetic field, and c the torsion constant of the fibre. For low temperature work the crystal is suitably suspended within the cryostat chamber and its anisotropy measured as above, at different temperatures. In the present measurements the crystals were usually chosen to have a large degree of geometric symmetry and the magnetic field being also highly homogeneous the effect due to the anisotropy of shape is negligible. The measurements of anisotropies of orthorhombic crystals were made by suspending the crystal successively with two of the principal axes vertical, observing the direction of setting in the magnetic field, and determining the difference between the maximum and minimum susceptibilities in the horizontal plane. For monoclinic crystals one suspension with 'b' axis vertical enables us to determine the directions of the principal susceptibilities χ_1 and χ_2 in the plane (010) *i.e.*, the angles ψ and θ between χ_1 and 'c' axes and between χ_2 and 'a' axes; and also the difference $\chi_1-\chi_2$. Measurement with one other suspension will give $\chi_1-\chi_3$ also. In general, since the (001) plane in the crystals used by us were well developed, this measurement was made either with the 'a' axis vertical, which gives

$$|\Delta\chi|=\pm[(\chi_1-\chi_3)-(\chi_1-\chi_2)\sin^2\theta] \qquad \ldots\ (11)$$

or with (001) plane horizontal, which gives

$$|\Delta\chi|=\pm[(\chi_1-\chi_3)-(\chi_1-\chi_2)\cos^2\theta] \qquad \ldots\ (12)$$

the positive or negative sign being chosen in the equations according to as the 'b' axis sets perpendicular or parallel to the magnetic field in the above suspensions. Occasionally, the second measurement of anisotropy was made with the well developed (201) plane vertical and 'b' axis horizontal. With each suspension the measurements of anisotropies of the crystals were made from room temperature down to about 80°K and back again to room temperature at intervals of about 25°, thus providing a check.

4. *Measurement of Absolute Susceptibilities*

The absolute susceptibilities were measured by suspending the crystal in an inhomogeneous magnetic field with a vertical gradient, from one arm of a

sensitive torsion microbalance of special design (Bose, 1948) and measuring the vertical force on the crystal with the balance. As shown in the earlier paper

$$\frac{F_T}{F_\Theta} = \frac{\chi_T}{\chi_\Theta}\left[1 + \frac{k_{a\Theta}}{k_\Theta}(1+\gamma(\Theta))\left(1-\frac{\Theta}{T}\right)\right] \qquad \ldots (13)$$

where F_T and F_Θ are the vertical forces on the crystal at any temperature T and room temperature Θ respectively, temperatures being measured on the absolute scale, χ_T and χ_Θ are the corresponding gram molecular susceptibilities of the crystal along the direction of the field, which in this region is horizontal; $k_{a\Theta}$ the volume susceptibility of air and k_Θ that of the crystal in the field direction both at room temperature; and γ is the coefficient of thermal volume expansion of the crystal. Thus if the forces at different temperatures are measured, knowing the absolute susceptibility of the crystal in the direction concerned at room temperatures, the values at other temperatures can be calculated. In actual practice, the crystal was suspended from one arm of the torsion balance within the cryostat chamber, placed in the inhomogeneous magnetic field and the angle of torsion on the balance fibre necessary for balancing the magnetic force was noted at various temperatures.

5. *Experimental Results*

The values of anisotropies $\chi_1-\chi_2$ and $\chi_1-\chi_3$ at intervals of 20°C as obtained from graphical interpolation from actual experimental values are given in the Table II and plotted in Figs. 1-3.

Knowing the anisotropies of the crystal in this temperature range, the determination of absolute susceptibility along any one convenient direction in the crystal, at different temperatures in the same range, will serve to give uniquely all the three principal susceptibilities of the crystal at these temperatures. These principal susceptibilities are then corrected for the diamagnetism of the salt and the effective moments of the paramagnetic ion in the crystal for the three principal directions are calculated therefrom using the formula

$$\chi_i = \frac{N p_i^2 \beta^2}{3kT}, \quad i = 1,2,3 \qquad \ldots (14)$$

where χ_i is the corrected principal susceptibility per gm. ion, and p_i is the effective moment per ion in the direction concerned, expressed in terms of the Bohr magneton. The values of the effective moments thus calculated are given in Table III and plotted in the insets of Figs. 1-3. The variations of the effective moment represent uniquely the deviations from the 'free ion behaviour' and therefore form suitable basis for discussion of the observed paramagnetic behaviour of crystals on the crystalline electric field theory. Since, the variations of the effective moments were not very large and no singularities or discontinuities were observed in the magnetic behaviour for any of the crystals

studied here, a determination of the absolute susceptibilities at three different temperatures was sufficient to give the temperature variations of the effective magnetic moments within this range correctly.

Table I gives the values used for the diamagnetic corrections.

TABLE I

Ion or molecule	K_2SO_4	$(NH_4)_2SO_4$	SO_4^{--}	$(NH_4)_2BeF_4$	$6H_2O$	BeF_4^{--}	Cs_2Cl_4	Fe^{++}, Co^{++}, Ni^{++}, Cu^{++},
Value of Diamagnetic correction $\times 10^6$	−70.2	−77.8	− 33.6	−66.7	−77.7	−32.6	−162	− 13.0

TABLE II

For Principal Anisotropies of Crystals with Different Suspensions

$NiSO_4$ $(NH_4)_2SO_4 6H_2O$ Monoclinic, $\beta \equiv 107°4'$ $a:b:c = 0.7370:1:0.5032$.				$NiSO_4$. K_2SO_4. $6H_2O$ Monoclinic, $\beta = 105°0'$ $a:b:c = 0.7379:1:0.5020$.				$NiBeF_4$. $(NH_4)_2BeF_4$. $6H_2O$ Monoclinic; $\beta = 106°40'$ $a:b:c = 0.737:1:0.491$.			
(1) 'b' axis vertical (2) 'a' axis vertical 'b' axis normal to field.				(1) 'b' axis vertical (2) 'a' axis vertical 'b' axis normal to field.				(1) 'b' axis vertical, (2) 'a' axis vertical, 'b' axis normal to field.			
Temp °K.	Angle* between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp °K.	Angle * between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$	Temp °K.	Angle * between 'a' axis & χ_2 axis $= \theta$	$\chi_1 - \chi_2$ $\times 10^6$	$\chi_1 - \chi_3$ $\times 10^6$
303.1	31	110.0	106 2	303.1	27	158 0	152.6	299.1	31	107.0	103 4
280	32	120.0	116.9	280	27	174 0	166.4	280	30.5	114.5	110.1
260	32 5	130 0	126.9	260	27	190.3	181.3	260	30	124 3	119.0
240	32.75	143.0	139.1	240	27	209.9	199.8	240	30	136.7	131.8
220	33	158.2	154.7	220	27	233.8	223.4	220	30	152.6	147.8
200	33 25	177 6	173 7	200	27	263.2	252.9	200	30	172 1	168.2
180	34.5	203 0	200.6	180	27	301.7	291.8	180	30	195.2	195.1
160	35.5	236 0	235.4	160	27	350.9	340.8	160	30	234.2	230.2
140	36	281.1	281 7	140	27	426.7	406.9	140	30	282.4	279.7
120	36.25	349.3	350.1	120	28	545 1	501.4	120	30	354.6	353 2
100	36.25	454.4	453.7	100	28	717.4	672.8	100	30	454.5	446.7
90	36.25	533.5	533.3	90	28	813.4	772.7	.....	...	...	...
86.6	36.25	565.8	564.3	86.6	28	857.8	812.8	84.7	30	547.0	531.3

*Angle measured in degrees.

TABLE III

For the Gm. Molecular Principal Susceptibilites and the Squares of the Effective Magnetic Moments. (*Corrected for Diamagnetism*).

Crystal	Crystal suspension and the direction along which the susceptibility is measured, *i e* the direction setting along field	Temp °K.	χ_1 $\times 10^6$	χ_2 $\times 10^6$	χ_3 $\times 10^6$	p_1^2	p_2^2	p_3^2	p^2
$NiSO_4(NH_4)_2$ $SO_4, 6H_2O$	'*b*' axis vertical, 'χ_1' axis along field	297 5	1315	1202	1206	10 34	10 07	10.08	10.16
		167 9	7520	7298	7300	10 17	9.870	9 872	9.971
		86 6	14112	13846	13818	10.06	9 661	9 663	9.795
$NiSO_4K_2SO_4$, $6H_2O$	(001) plane horizontal '*a*' axis along field	297.1	1350	1188	1191	10 42	10 03	10 05	10 17
		173 1	7171	7155	7165	10 43	9 993	10 01	10 14
		86 6	11633	13775	13820	10 21	9 610	9 642	9 821
$NiBeF_4(NH_4)_2$, $BeF_4, 6H_2O$	'*b*' axis vertical, 'χ_1' axis along field	297 1	4351	1216	1250	10 13	10.17	10 18	10 26
		172 2	7391	7180	7183	10.25	9 959	9 963	10 06
		84 7	14777	11230	11246	10.08	9 709	9 721	9 837

DISCUSSION OF RESULTS

1. *The Directions of the Principal Magnetic Axes in Relation to Asymmetry of the Crystalline Electric Field*

In the paramagnetic crystals that we are considering the paramagnetic behaviour, as we have seen, is largely affected by the electric field acting on the paramagnetic ion, arising from the surrounding negatively charged atoms. It has been shown by Van Vleck (1932), Bethe (1929), Penney and Schlapp (1932) and others, that in most cases the deviation of the paramagnetic ion from 'free ion' behaviour may be explained by the simple postulate of a predominantly cubic field with a small rhombic component superposed upon it, acting on the paramagnetic ion. Thus the potential V, of the electron in this crystalline field may be represented as a Taylor series, about the centre of the paramagnetic ion, the non-vanishing terms in which are given by

$$V = Ax_1^2 + By_1^2 - (A+B)z_1^2 + D(x^4 + y^4 + z^4) + 3Dr^4 \quad \ldots \quad (15)$$

in which the squared and fourth power terms represent the rhombic and the cubic parts of the field respectively. The last term need not be considered further, since it represents the spherically symmetric part of the field and does not change the relative separations of the levels in the Stark-pattern produced by the field.

In general the x, y, z axes of the rhombic and the cubic parts do not coincide each to each, though for our purpose it is found to be enough to assume that they do coincide. Whenever experimental data make it necessary to have a field of lower symmetry we can construct it by suitably orienting the two sets of axes.

A further complication in the analysis of the behaviour of paramagnetic ion arises due to the fact that the unit cell of the crystal will in general

contain more than one ion with their field axes oriented with respect to one another and a knowledge of these orientations is generally not available. The crystalline field axes associated with each ion are uniquely determined by the dispositions of the surrounding negatively charged atoms and presumably will not change since the paramagnetic ion is strongly bound to the neighbouring charged atoms, as evidenced by the large over-all Stark separation of the energy levels of the order of 20,000 cm^{-1}. Further evidence of such strong binding is obtained from the persistence of such ionic groups even in the state of solutions which explains the large deviations from the 'free ion' behaviour observed in the aqueous solutions of many of the salts of the iron group.

The binding between the different ionic groups may, however, be relatively much weaker and the groups may therefore change their orientations with respect to one another as temperature changes, causing an appreciable change in the position of the magnetic axes of the crystal where they are not already fixed by crystal symmetry. Actually such changes have been observed by us though these are very small except in a few cases. A detailed account of these has been published in an earlier paper (Bose, 1947).

In any case it may be safely concluded that the electric field in the neighbourhood of the paramagnetic ions are practically unaffected by the changes in temperature. This is further corroborated by a detailed calculation to be given later, of the crystal field constants in such favourable cases as the six-coordinated nickel salts and the four-coordinated cobalt salts. A further point which emerges from these considerations is that not only the predominant cubic part of the field but also the feeble rhombic part will be determined by the immediate neighbours, the effect of more distant charged atoms being negligible. This point of view apart from its plausibility considerably simplifies the problem of correlating the magnetic behaviours of the *ion* and the *crystal*.

2. *Nature of Stark-pattern under Crystalline Field for Different Ground States and its Effect on the Magnetic Behaviour*

In the iron group of elements we are concerned with the S, D and F-state ions only, in which the coupling between the orbital and the spin momenta of the *3d* electrons, responsible for the paramagnetism of the ions, is of the Russel-Saunders type. The crystalline fields involved in the *ionic salts* of these ions are sufficiently strong to break the *l-s* coupling but not strong enough to break the *l-l* or the *s-s* couplings, so that we can discuss the effect of the crystalline fields upon the L and S moments of the ions separately. Since the spin moments are not much affected by the crystalline fields, the behaviour of the S-state ions *e.g.*, Mn^{++} and Fe^{+++}, where the entire magnetic moment is due to the spins, will be simple as has been already mentioned in a previous section.

General behaviour of the other ions of the iron groups will be evident from what follows. Neglecting for the present any effect of the crystalline

fields upon the spin energy levels of the ions, the Stark-pattern of the ions in these electric fields would correspond to the removal, either partly or wholly, of the $(2L+1)$-fold orbital degeneracy. How complete is the removal of the orbital degeneracy will depend upon how asymmetric the field is. For example, in a field of cubic symmetry the D-state splits up into a doubly degenerate and a triply degenerate level ; and an F-state into a singlet and two successive triply degenerate level. With the large cubic fields involved in these crystals, the over-all separation of the above cubic Stark-patterns will be of the order of 10^4 cm^{-1}. A small rhombic field superimposed on the cubic field will naturally separate the components of the individual doublet or triplet but to a much smaller extent than the cubic separations. Each one of these various levels will, in the absence of a strong spin-orbit coupling, retain its $(2S+1)$-fold spin degeneracy, which can be removed by the application of the magnetic field and will lead to the magnetization of the medium. In general, however, though the spin moments are very little affected by the electric fields directly,* still owing to the coupling of these moments with the orbital moments, there will be an appreciable separation of the spin components also, by the rhombic field. The width of this spin Stark-multiplets will depend upon the strength of the rhombic field and the spin-orbit coupling.†

Since the Stark-pattern of the F-state corresponds to two adjacent triplets and a singlet, the energy of the singlet state should be either the highest or the lowest in the pattern. Which it is will depend upon the nature of the cubic part of the crystalline field. This point is of great interest and will be discussed in a part of the paper to be published later on. If the singlet level is the lowermost, since the triplets will be far removed from it, cubic separation being of the order of 10^4 cm^{-1}, practically the singlet level alone will be occupied at all ordinary temperatures.‡ Since this level retains almost all its $(2S+1)$-fold spin degeneracy in the crystalline field, the ion will behave very nearly like S-state ions, in having a feeble anisotropy, nearly spin only value of the effective moment and small deviation from the Curie Law.

In the D-state ions on the other hand, the lowest state in the cubic field has to be either the doublet or the triplet, the separation between the components of either of which, being produced by the feeble rhombic field, will be comparable to kT and the population of the upper components of the lowest level will be quite appreciable. The magnetic behaviour of these ions will

* Here we should not forget the very small 2nd order Kramers splitting of the spin-levels due to the direct effect of the electric fields on the spin moments.

† It should be mentioned here that when the number of electrons in the incomplete shell is odd, there will be a two-fold Kramers spin degeneracy that will always be left over, however large the spin-orbit coupling may be.

‡ We shall see later on that the populations of the upper levels are not negligible and these levels also contribute appreciably to the total magnetisation through the temperature-independent " high frequency" terms.

not therefore be so simple as that of the F-state ions with the singlet level lying lowest. In general, the behaviour of the F-state ions with the triplet lying lowest and the D-state ions will be complicated and will be dealt with in subsequent parts of the paper.

3. *Ionic Salts of Cr^{+++} and Ni^{++}*

In the six-co-ordinated salts of Cr^{+++} and Ni^{++} ions, of which the ground states are $^4F_{3/2}$ and $^3F_4$ respectively, the singlet level is the lowest. This corresponds, as shown by Van Vleck (1932) and Görter (1932) to the cubic field constant D in the expression (15) being positive. It has been shown (1) that the crystalline field in these salts may be usually represented by a predominant cubic part with a superimposed small rhombic component such that the principal axes of the former are coincident, respectively, with those of the latter, so that the field potential may be represented by

$$V=D\,(x^4+y^4+z^4)+Ax^2+By^2-(A+B)z^2. \qquad \ldots \quad (16)$$

It is assumed further (2) that the crystal field axes for all the paramagnetic ions in the crystal are parallel to one another.* Penney and Schlapp (1932) have calculated the principal susceptibilities of the crystal in terms of the field constants and the spin-orbit coupling constant λ, for the free ion, obtained from the over-all multiplet width for the free ion (Laporté, 1928),

$$W=\lambda.S(2L+1). \qquad \ldots \quad (17)$$

The three principal susceptibilities of the crystals, evidently measured along the co-ordinate axes x, y, z, and the corresponding effective magnetic moments may be given by

$$\chi_i=\frac{N\beta^2}{3k'T}p_i^2, \quad i=1, 2, 3 \qquad \ldots \quad (18)$$

where according to Penney and Schlapp

$$p_i^2=p_0^2\left[1+8\lambda\alpha+\frac{\Delta_i\lambda^2}{kT}+\ldots\ldots\ldots-3kT\alpha\right], \qquad \ldots \quad (19)$$

where $p_0^2=4S(S+1)$, p_0 being the 'spin only' value of the moment and related to the corresponding susceptibility by

$$\chi_0=\frac{N\beta^2}{3kT}p_0^2; \qquad \ldots \quad (20)$$

also,

$$\Delta_1=\tfrac{2}{3}(\alpha_2+\alpha_3-2\alpha_1) \qquad \ldots \quad (21)$$

and two similar expressions for Δ_2 and Δ_3. The α's are functions of crystalline field constants D, A and B. The mean susceptibility of the crystal

* This will be the case when the unit cell of the crystal contains only one paramagnetic ion. Though assumption (2) is not explicitly stated by Penney and Schlapp, it is at the basis of all their calculations.

is given by

$$\lambda = \frac{N\beta^2}{3kT} p^2, \qquad \ldots (22)$$

where $$p^2 = \tfrac{1}{3}(p_1^2 + p_2^2 + p_3^2) = p_0^2 [1 + (\alpha_1 + \alpha_2 + \alpha_3)(\tfrac{8}{3}\lambda - kT)]. \qquad \ldots (23)$$

4. *Magnetic Behaviour of Nickel Salts; Calculations of Spin-orbit Coupling and Field Constants*

Calculations of the field constants D, A, B and α's in various Ni^{++} salts, from magnetic data at room temperature by Krishnan and Mukherji (1938), gives us an idea regarding the relative importance of the effects of the cubic and rhombic parts of the field on the magnetic behaviour.

Taking for the Ni^{++} ion the spin-orbit coupling constant $= -335$ cm^{-1} calculated from its over-all multiplet width 2347 cm^{-1} as given by Laporte and values of α's given by us in Table V, we have calculated the values for the different terms in the expressions (19) for the effective moments along the three principal axes, for the crystal of $NiSO_4(NH_4)_2SO_4$, $6H_2O$ as an example, to exhibit the relative importance of the different terms. At room temperature, namely 303.1°K :

$$p_1^2 = p_0^2 [1 + 8\lambda\alpha_1 - 3kT\alpha_1 + \frac{\Delta_1\lambda^2}{kT} + \ldots\ldots]$$

$$= 8[1 + .2268 + .0527 + .0054] = 10.28$$

and similarly,

$$p_2^2 = 8[1 + .2064 + .0480 - .0028] = 10.01$$

$$p_3^2 = 8[1 + .2066 + .0480 - .0027] = 10.02 \qquad \ldots (24)$$

It will be seen at once that the last terms in the above expressions are quite negligible at room temperature and indeed vanishes altogether for the mean square moment. Of the others, the temperature independent terms, namely, $1 + 8\lambda\alpha_i$ greatly predominate, since the term $3kT\alpha_i$ is less than 5% of $1 + 8\lambda\alpha_i$. Thus, it will be seen at these temperatures : (1) that

$$\frac{p_1^2 - p_0^2}{p_0^2} \sim 8\lambda\alpha_1 - 3kT\alpha_1 \sim .23 + .05 = .28, \qquad \ldots (25)$$

i.e., for a nickel salt the square of the effective magnetic moment in any particular direction, say p_1^2, and hence the principal as also the mean susceptibilities may be as much as 28% higher than the 'spin only' value ; (2) on the other hand p_1^2 will change little with temperature and hence the three principal susceptibilities of the crystal and *a fortiori* their mean will conform closely to the Curie Law ; (3) lastly, since the three α's differ from one another by only about 10% and the terms involving the α's account for less than a fourth part of the moments, the anisotropy of the crystal, $(\chi_1 - \chi_2)/\chi = (p_1^2 - p_2^2)/p_2^2$ should be only 2 or 3% and thus quite feeble.

From the expressions (19) for p_i^2 it will be seen that, of the two terms $-3kT\alpha_i$ and $\frac{\Delta_i\lambda^2}{kT}$ involving temperature the first is positive since α_i is

negative, and decreases with temperature for all the three principal moments, whereas, the second is positive for p_1^2 but negative for p_2^2 and p_3^2 and increases in magnitude with decrease of temperature for all the Ni^{++} salts studied by us. Thus p_1^2 goes on diminishing as the temperature falls, but at a decreasing rate as the last term becomes more and more important, until at a temperature somewhat below 80°K, the value of p_1^2 reaches a minimum and then increases again. The values of p_2^2 and p_3^2 on the other hand, go on falling at gradually increasing rate as temperature decreases. Though, unfortunately our data could not be extended below 80°K to verify these interesting calculations in all details, the experimental values fit in extremely well within the present range of temperatures with those theoretically calculated, as will be seen from Table III and the graphs for p_1^2 for the three Ni^{++} salts.

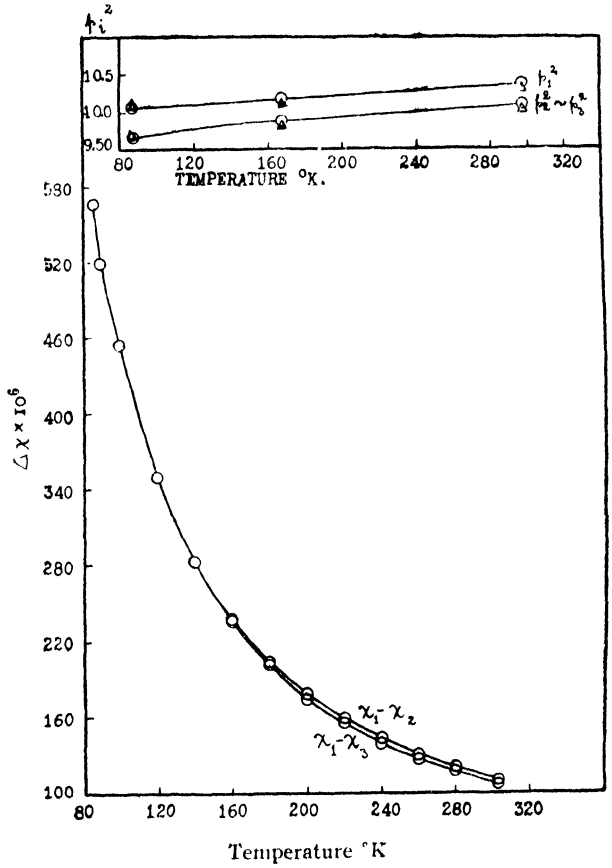

FIG. 1

Temperature Variation of Principal Anisotropies and Effective Moments of $NiSO_4(NH_4)_2SO_4.6H_2O$

Reverting to the expression (19) it will be seen that the excess of the effective magnetic moment over the 'spin only' value, is mainly due to two

causes. A small part of this excess is due to the term $-3kT\alpha_i$, which corresponds to the temperature independent part of the susceptibility, and can

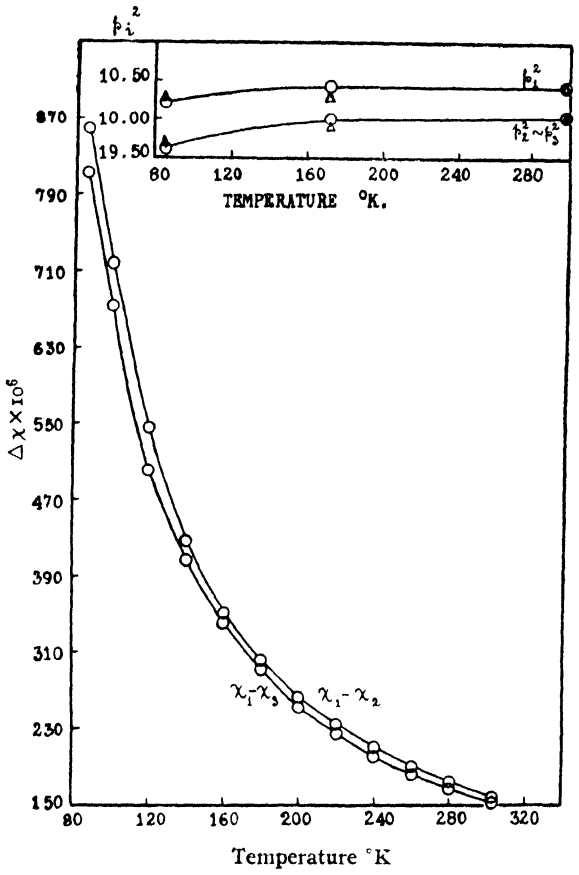

FIG. 2

Temperature Variation of Principal Anisotropies and Effective Moments of $NiSO_4.K_2SO_4.6H_2O$

be traced ultimately to the influence of the upper levels in the Stark-pattern. But the bulk of it, represented by the term $8\lambda\alpha_i$, can be traced to the indirect effect on the spin moments of the electric field, through the spin-orbit coupling, and thus dependent on the value of λ. At low temperatures of course, the value of the second order spin term $\frac{\Delta_i\lambda^2}{kT}$, becomes also highly important; but in the present range it is more or less negligible.

Conversely, it should be possible, from these deviations from "spin only" value, to calculate the constant of spin-orbit coupling λ, purely from magnetic data, since the field constants α, may be regarded as practically independent of temperature, for reasons previously stated, and may thus be eliminated using data at different temperatures. Since in the expression for p_i^2 or p^2 the term involving λ is fairly large, about 23% of the other terms, it might appear at first that the variations of the effective moments with temperature

should serve us conveniently to eliminate the α's. It is, however, found that this is not so, since the term involving λ, though large, is independent of the

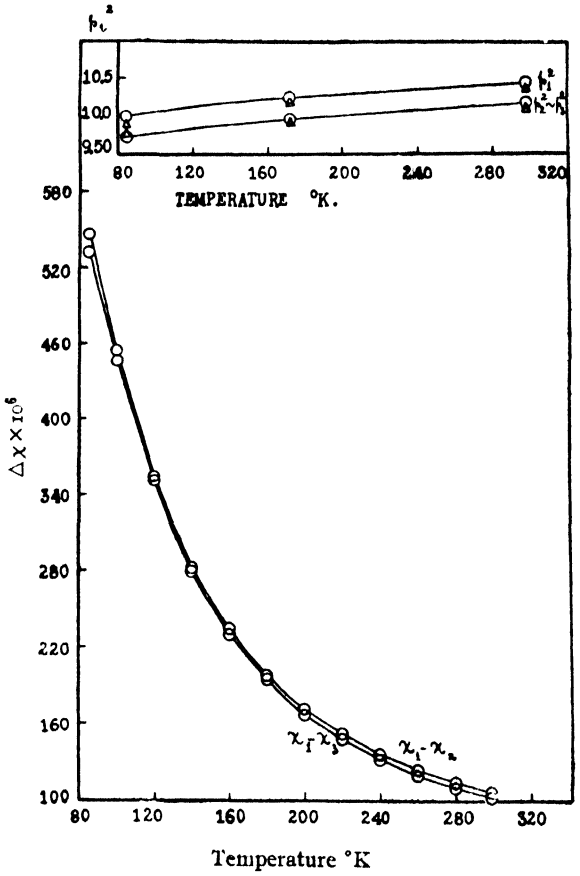

FIG. 3

Temperature Variation of Principal Anisotropies and Effective Moments of $NiBeF_4(NH_4)_2\ BeF_4.6H_2O$

temperature. On the other hand, in the expression for anisotropy $\Delta\chi$, for any selected plane in the crystal, namely,

$$\frac{\Delta\chi}{\chi_0} = \frac{\Delta p^2}{p_0^2} = \left[8\lambda - \frac{2\lambda^2}{k'T} - 3k'T \right] \Delta\alpha, \qquad \ldots \quad (26)$$

where $\Delta\alpha$ will be a constant depending on the crystalline field and the crystal plane chosen, the temperature independent last term in the *absolute susceptibility* will be largely suppressed. For example, for Ni^{++} at room temperature 300°K say, all the three terms are negative and are respectively, of the order of -0.026, -0.010 and -0.006. The λ^2 term is not negligible as in the expression for effective moment. Indeed, even at room temperatures it is nearly twice the term independent of λ and at 80°K becomes about 25 times this term and comparable in magnitude with the temperature indepen-

dent first term in the *anisotropy*. Thus the measurement of anisotropy at different temperatures is more suitable for the calculation of λ.

In a previous paper (1938-39) we obtained in this manner from anisotropy measurements of the salts $NiSO_4,6H_2O$ and $NiSeO_4,6H_2O$ the values of $\lambda = -330$ cm^{-1} and -340 cm^{-1} respectively, agreeing satisfactorily with the spectroscopic value of -335 cm^{-1}. In the Table IV will be found the values of λ, for various other nickel salts studied by us, fitting with the anisotropy measurements over the whole range of temperature. The mean value of λ, for different crystals and different crystal planes is found to be about -350 cm^{-1}, agreeing fairly well with the spectroscopic value and is indeed gratifying.

It may be mentioned here that though the temperature variations of the effective moments are not so suitable as those of the anisotropies for calculating λ, they are still fairly consistent with the values of λ, calculated in the latter manner.

TABLE IV

Ratio of $\Delta\chi$ at temperatures T to that at room temperature (303.1°K)

Salts	$NiSO_4$, $(NH_4)_2SO_4$, $6H_2O$				$NiSO_4K_2SO_4$, $6H_2O$				$NiBeF_4(NH_4)_2BeF_4$, $6H_2O$			
Ratio obtained from anisotropies	$\chi_1-\chi_2$		$\chi_1-\chi_3$		$\chi_1-\chi_2$		$\chi_1-\chi_3$		$\chi_1-\chi_2$		$\chi_1-\chi_3$	
Values of λ	-315 cm^{-1}		-348 cm^{-1}		-370 cm^{-1}		-360 cm^{-1}		-345 cm^{-1}		-360 cm^{-1}	
Temperature °K	Ratio		Ratio		Ratio		Ratio		Ratio		Ratio	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc	obs.	calc.	obs.	calc.
303.1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
240	1.300	1.298	1.310	1.310	1.328	1.316	1.309	1.313	1.289	1.308	1.287	1.313
200	1.614	1.614	1.636	1.640	1.665	1.654	1.658	1.648	1.624	1.638	1.643	1.648
160	2.145	2.144	2.217	2.191	2.221	2.229	2.234	2.213	2.210	2.191	2.248	2.213
100	4.131	4.127	4.273	4.289	4.539	4.398	4.410	4.349	4.288	4.278	4.362	4.349
90	4.850	4.828	5.021	5.036	5.147	5.171	5.064	5.111	—	—	—	—

The agreement between the observed and calculated values entered in Table IV, shows that for a given crystal and crystal directions a single value of λ, fits well over the whole range of temperature. This result may be taken to confirm the assumption on which these calculations are based, namely, that the magnitude and asymmetry of the crystalline field should be independent of temperature, which was made from considerations regarding the strong binding between the paramagnetic ion and its immediate neighbours and the consequent

approximate non-variance of their positions with changes of temperatures. A direct calculation of the three α's at different temperatures, from the three principal susceptibilities of the nickel salts studied by us, also leads to the same conclusion, namely, that the α's are practically independent of temperature as will be seen from the Table V.

TABLE V

For the crystal Field Constants α_1, α_2 *and* α_3 *for* Ni^{++} *Salts*

Crystal	Temp. °K	$-\alpha_1 \times 10^6$	$-\alpha_2 \times 10^6$	$-\alpha_3 \times 10^6$
$NiSO_4(NH_4)_2SO_4 . 6H_2O$	297 5	85.7	78 o	78.3
	167.9	85.4	77.8	77.9
	86 6	82 7	75 2	75.2
$NiSO_4K_2SO_4 . 6H_2O$	297.4	88.2	77.2	77.5
	173 4	94.7	83 4	83.8
	86.6	86.4	75.0	75.6
$NiBeF_4(NH_4)_2BeF_4 . 6H_2O$	297 4	89.2	81.8	82.1
	172 2	88.9	81.4	81.6
	84 7	84.9	77.9	78.1

It may be mentioned here that these calculations of α's are not merely the converse of that of λ, which would have been then a trivial result. The information conveyed by these two calculations are quite different not only because the measurement of *principal susceptibilities*, from which α's are calculated, are independent of the measurements of *anisotropies*, from which λ is calculated, but also the relative importance of the terms corresponding to the oth, 1st and 2nd powers of λ, involved in these two calculations are quite different.

5. *Chromic ion : Close Approximation to S-State Ions Regarding Magnetic Properties.*

For the Cr^{+++} ion with three electrons in the $3d$ shell, λ is positive, unlike Ni^{++} with 8 electrons in the $3d$ shell and its numerical value calculated from the over-all multiplet width of 912 cm^{-1} (Laporte, 1928), is $\lambda = +87\ cm^{-1}$, much smaller than for Ni^{++} ion. These two factors together completely alter the relative importance of the different terms in the expression for p^2, as compared to that of Ni^{++}. Taking α's to be of the same order of magnitude as in the ionic salts of nickel, we obtain for the mean susceptibility at 300°K.

$$p^2 = p_0^2[1 + (\alpha_1 + \alpha_2 + \alpha_3)(\tfrac{8}{3}\lambda - kT)] = 15[1 - .058 + .052] \quad \ldots \quad (27)$$

Here the last two terms, which represent the deviation of the effective magnetic moment from its 'spin only' value, are both small, of comparable magnitudes

and of opposite signs.* Hence the deviation from the 'spin only' value becomes very small, being about ½% smaller at room temperature and about 4½% at 80°K.

Our measurements for chromic salts refer to room temperature only, where 'spin only' value is approximately obtained (Krishnan, Mukherji and Bose, 1939).

We should further expect from the theoretical expressions, the anisotropy of the crystal to be smaller and the conformity to Curie Law much closer than even in the nickel salts. Indeed, the anisotropies of the chromic salts are nearly of the same magnitude as the anisotropy of the diamagnetic part of the susceptibility of these crystals, as will be seen from the table VI by comparison of the data for the isomorphous salts, ammonium chromium oxalate and potassium aluminium oxalate the latter being diamagnetic. In view of this it becomes difficult to verify even the $1/T^2$ law, deduced theoretically for the temperature variation of the paramagnetic part of the anisotropy.

TABLE VI

Anisotropies at 303.1°K

Anisotropies × 10^6	$(NH_4)_3\,Cr(C_2O_4)_3,\ 3H_2O$ $a : b : c = 0.983 : 1 : 0.387$	$K_3Al(C_2O_4)_3,\ 3H_2O$ $a : b : c = 0.999 : 1 : 0.395$
$\chi_1 - \chi_2$	4.3	7.9
$\chi_1 - \chi_3$	−10.3	13.9
ψ	29°	19°

Further, approximate calculations for the value of λ, for the Cr^{+++} ion from the above experimental data agree in order of magnitude with the spectroscopic value. A more detailed experimental investigation on Cr^{+++} salts is in progress in this laboratory in view of the inadequacy of existing experimental data.

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* That these two terms in Cr^{+++} are of comparable magnitudes and of opposite signs, and that neither of them can be neglected, needs to be emphasised here in view of the fact that in the expression given by Penney and Schlapp (*loc. cit.*) the kT term is neglected, whereas a term proportional to λ^2, which indeed should vanish in the expression for the mean square moment, is retained.

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